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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Crivello, James V. and Carlson, Kenneth D.(1996) 'Photoinitiated Cationic Polymerization of Naturally Occurring Epoxidized Triglycerides', *Journal of Macromolecular Science, Part A*, 33: 1, 251 – 262

To link to this Article: DOI: 10.1080/10601329608020381

URL: <http://dx.doi.org/10.1080/10601329608020381>

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PHOTOINITIATED CATIONIC POLYMERIZATION OF NATURALLY OCCURRING EPOXIDIZED TRIGLYCERIDES

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ABSTRACT

Naturally occurring epoxidized triglyceride oils were obtained from two plant sources: *Vernonia galamensis* and *Euphorbia lagascae*. Samples of the oils were subjected to UV induced cationic photopolymerization in the presence of a diaryliodonium salt photoinitiator. The rates of the photoinduced cationic polymerization of the oils were investigated as a function of the source of the oil and the concentration of the photoinitiator and also compared with a chemically epoxidized triglyceride, epoxidized soybean oil.

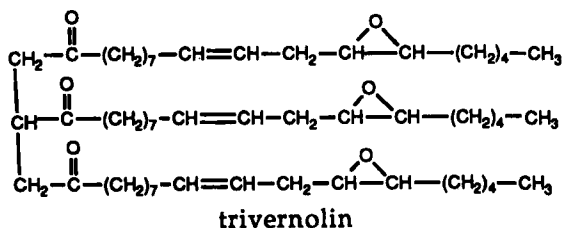
INTRODUCTION

Monomers derived from naturally occurring substrates represent a potential future growth area for both plastics and agriculture. Ideally, such

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substrates should be readily isolated in high yields from easily grown plant species and then used directly in polymerization reactions to make polymers. In this communication, we describe development efforts currently in progress which may make this possible.

Over the past three decades, considerable research has been directed towards the development of new oilseed crops. Of particular interest has been the identification and cultivation of plant species which are capable of producing epoxidized triglycerides [1, 2]. Among the dozen or so species that have been identified to possess this characteristic, two plants, *Vernonia galamensis* [3 -7] and *Euphorbia lagascae* [8] have received the most attention and are currently being developed for domestication. Both plants produce triglyceride oils containing vernolic acid (cis-12,13-epoxy-cis-9-octadecenoic acid) residues, of which trivernolin (glyceryl trivernolate) shown below is a major component.



Extraction of the seeds of *V. galamensis* yields 40-42% oil by weight of the seeds of which vernolic acid residues comprise 78-80%. Similar treatment of *E. lagascae* seeds gives a 52% yield of oil of which vernolic acid residues comprise 60%. Thus, these two plant species are rich sources of vegetable oils as compared to soybeans in which the triglyceride oil comprises only 18-20% of the dry weight of the seeds. Given in Table 1 is data comparing the triglyceride oils from *V. galamensis* and *E. lagascae* with epoxidized soybean oil, which is produced commercially by peracetic acid epoxidation of the native oil.

Table 1 Characteristics of Epoxidized Triglyceride Oils

Triglyceride Oil	Oil content in seeds (%)	W.P.E. ^a	Epoxy Number ^b
<i>Euphorbia lagascae</i>	52	466.7	3.4
<i>Vernonia galamensis</i>	40-42	350.0	4.6
Epoxidized soybean	18-20	223.8	7.1

^a Weight per epoxide equivalent. ^b% Oxirane oxygen.

The prospects of employing epoxidized natural triglyceride oils for coatings has attracted much attention recently. Dirlikov and his coworkers [9, 10] have reported the use of *V. galamensis* oil in air drying alkyd paints. Of particular interest to us is the observation that both natural and synthetic epoxidized oils can be photopolymerized in the presence of such cationic photoinitiators as diaryliodonium salts [11]. In this communication, we report recent work describing the cationic photopolymerization of both *V. galamensis* and *E. lagascae* oils and their comparison with epoxidized soybean oil.

EXPERIMENTAL

Materials

V. galamensis oil was obtained from two sources; Ver-Tec, Inc. (S1) and Rhone-Poulenc (S2). A sample of *E. lagascae* oil was obtained from the U.S. Dept. of Agriculture, Agricultural Research Service, Midwest Area. Epoxidized soybean oil was a gift of Elf-Atochem North America. All epoxidized oils were used as received without further purification. The synthesis of the

photoinitiator, (4-n-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10) was described previously [12].

Photopolymerization Studies

Thin Film Polymerizations

Thin films (~25 mm) of the liquid monomers (epoxidized oils) containing 2% of IOC10 photoinitiator were drawn onto glass panels and irradiated using a Fusion Systems 300 W microwave activated medium pressure mercury arc lamp mounted at a distance of 10 cm from the sample. This apparatus was equipped with variable speed conveyor which could be used to expose the samples to UV irradiation for various lengths of time.

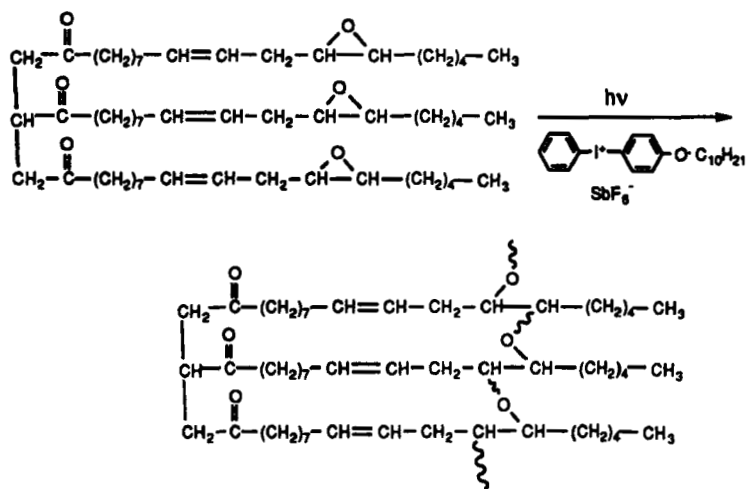
Fourier Transform Real-Time Infrared Spectroscopy (FT-RTIR)

Kinetic and conversion data for the cationic photopolymerization of the monomers were obtained using Fourier transform real-time infrared analysis (FT-RTIR). This method involves the monitoring of an appropriate IR band due to the polymerizing group while simultaneously irradiating the thin film sample with UV light. Measurements were performed on a Midac Series M Fourier Transform Infrared Spectrometer equipped with a liquid nitrogen cooled MCD detector. The instrument was fitted with a UVEXS Co SCU 110 UV lamp equipped with a flexible liquid optic cable directed at a 45° angle onto the sample window. All studies were conducted using broad band, unfiltered UV light at an intensity of 673 mJ/cm².min. Samples were prepared by placing the liquid monomer containing various concentrations of IOC10 between two poly(ethylene) films and then mounting the sandwich in 5 cm x 5 cm slide frames. The progress of the polymerizations was determined quantitatively by monitoring the decrease of the epoxide absorption at 825 cm⁻¹. The data was collected on a Bit-Wise Co. 486 PC computer, reduced and plotted as conversion versus time curves with the aid of a Galactic Industries Corp. Grams 386, Version 3.0 software package. Light intensity measurements were made with the aid of an International Light Co. Control-Cure Radiometer.

RESULTS AND DISCUSSION

Radiation curing, i.e., photo- and electron-beam induced crosslinking polymerization has become an important technique for curing coatings, inks and adhesives in existing manufacturing applications. Inherent advantages of radiation curing, compared to traditional thermal methods, are higher throughput rates and lower energy requirements. An added advantage of radiation-curable high-solids substrates is their low volatile organic compound (VOC) content and, therefore, low impact on air and water quality during their conversion to finished products [13].

In this laboratory, we have focused on photo- and electron-beam induced cationic polymerizations. Employing an onium salt photoinitiator, a wide diversity of cationically polymerizable monomers can be rapidly and efficiently polymerized [14]. Such photoinitiators may also be employed to polymerize virtually all types of epoxide-containing monomers including epoxidized vegetable oils. Equation 1 depicts one of a number of possible pathways for the UV induced polymerization of trivernolin [11].



eq. 1

Polymerization involves the release of the "super" acid, hexafluoroantimonic acid, by photolysis of the diaryliodonium salt photoinitiator. This is followed by the rapid intra- and intermolecular ring-opening polymerization of the epoxy groups of trivernolin.

We have observed that both *V. galamensis* and *E. lagascae* oils are readily polymerized when irradiated in the presence of diaryliodonium salt photoinitiators. In this study the photoinitiator (4-n-decyloxyphenyl) phenyliodonium hexafluoroantimonate (IOC10) was employed because it is freely soluble in the epoxidized triglyceride oils to give homogeneous solutions. The photoinitiator was used as a 50% solution in propylene carbonate as a carrier. The triglyceride oils were separated from the seeds by solvent extraction and used without additional purification. The appearance of an individual oil differed considerably depending on the plant of origin and its commercial source. For example, *V. galamensis* oil obtained from Ver-Tech (S1) was colored pale yellow-green and appeared quite viscous while the same oil (S2) supplied by Rhone-Poulenc, although more deeply colored, had a very low viscosity. *E. lagascae* oil was a low viscosity, turbid fluid with a pronounced yellow-green color. Since these oils are derived directly from their natural sources and were not subjected to exhaustive purification, it is likely that they contain small amounts of a variety of impurities, some of which may be basic and behave as inhibitors for cationic polymerization. Nevertheless, it was of considerable interest to note that despite this, the oils underwent facile polymerization. This could be observed simply by spreading mixtures of the monomer as thin (25 mm) films onto glass plates and then irradiating them using a 300 W medium pressure mercury arc lamp. In the presence of 2% by weight IOC10, *V. galamensis* and epoxidized soybean oils polymerized to tack-free films after a 1 second UV exposure. Under the same conditions, *E. lagascae* oil remained only partially polymerized. Increasing the IOC10

concentration to 4% gave tack-free films after a 1 second exposure with this latter triglyceride oil.

Further experiments were carried out using Fourier transform real-time infrared spectroscopy (FT-RTIR) to allow a more detailed comparison of the reactivity of the two naturally derived epoxidized oils. Employing this technique, the disappearance of the 825 cm^{-1} IR band (epoxy absorbance) was monitored as a function of time as the UV induced cationic epoxide ring-opening polymerization takes place. After 400 seconds, the irradiation was terminated and the IR absorption data was converted to conversion and plotted versus the irradiation time.

In Figure 1 is shown a study of the polymerization of *E. lagascae* oil using 2 and 4% IOC10 photoinitiator. Induction periods were observed in both cases, indicative of the presence of small amounts of basic impurities that function as inhibitors for the cationic polymerization. Increasing the concentration of photoinitiator from 2 to 4% markedly reduces the induction period. It may also be noted that once the impurities have been consumed by the photogenerated acid, polymerization sets in and the rates of the polymerizations (given by the slopes) are identical and independent of photoinitiator concentration.

Figure 2 depicts a similar study conducted on a sample of *V. galamensis* oil. In this case, the curves are nearly identical indicating that increased photoinitiator does not result in an increased rate of polymerization. This oil is essentially free of inhibiting impurities since essentially no induction period is observed. Further, the final conversion (85-90%) is the same at both initiator concentrations.

Figure 3 compares the rates of polymerization of two samples of *V. galamensis* oil obtained from different commercial sources (S1 Ver-Tech, Inc., S2 Rhone-Poulenc). The curves of these two samples directly overlap one another indicating that their reactivity is essentially identical. This is despite

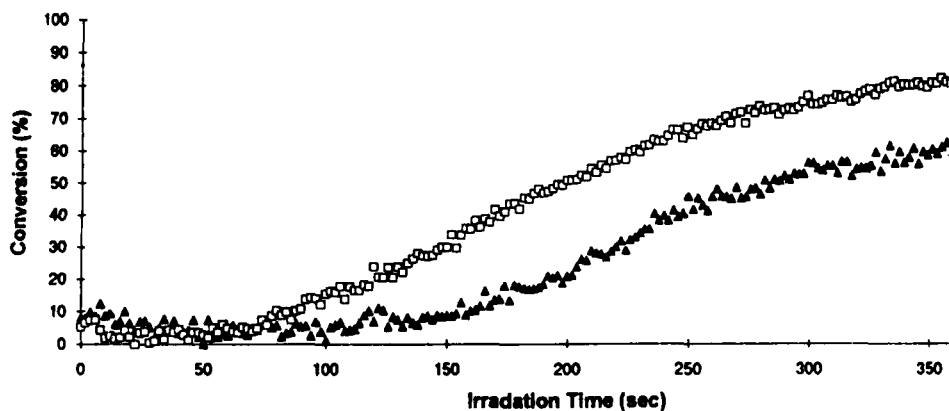


Figure 1. FT-RTIR study of the effect of IOC10 concentration on the photopolymerization of *Euphorbia lagascae* oil. ▲, 2%; □, 4% IOC10.

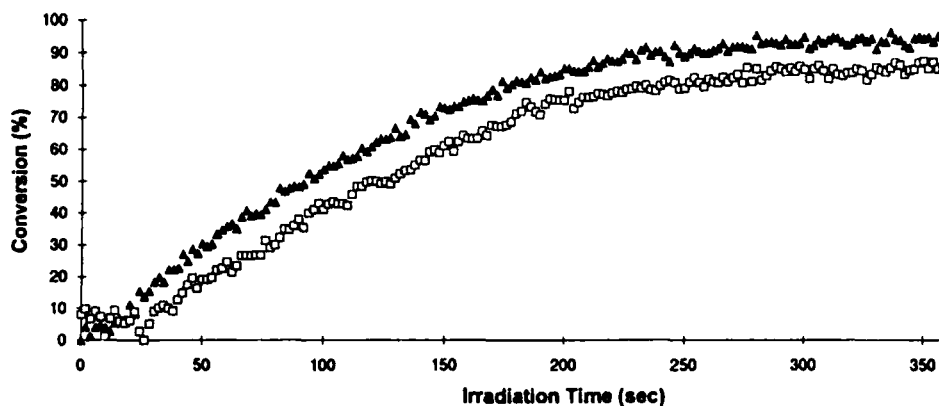


Figure 2. FT-RTIR study of the effect of IOC10 concentration on the photopolymerization of *Vernonia galamensis* oil. ▲, 2%; □, 4% IOC10

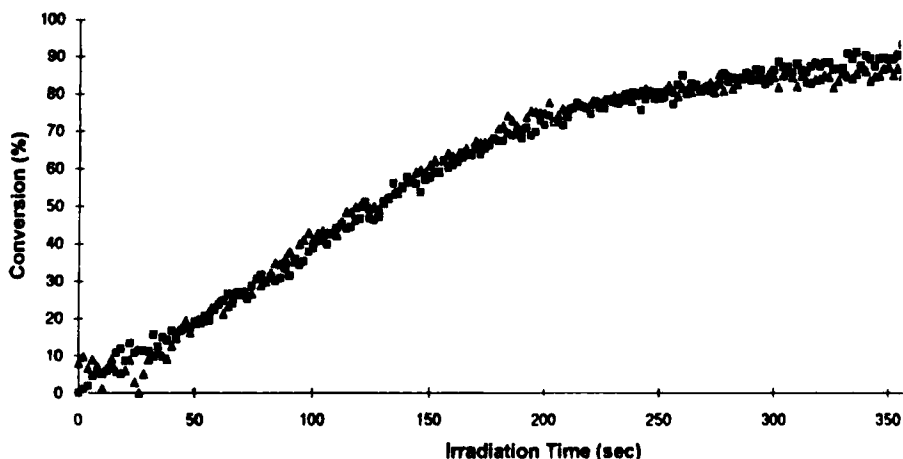


Figure 3. FT-RTIR curves for the cationic photopolymerization of *Vernonia galamensis* oil. \triangle , S1; \blacksquare , S2 in the presence of 2% IOC10.

the very different appearance of the samples with respect to their viscosity and color. S1 is highly viscous, possibly suggesting that during isolation and processing a small amount of some epoxide ring-opening to form alcohols has occurred. At the same time, S2 is a very low viscosity oil suggesting that little if any epoxide ring opening has taken place.

In Figure 4 is shown a direct comparison of *V. galamensis*, *E. lagascae* and epoxidized soybean oils at the same photoinitiator concentration (2%). The three oils display a markedly different response to photoinitiated cationic polymerization. Neglecting the differences in the inhibition period, *V. galamensis* and *E. lagascae* oils display essentially the same initial slopes indicating that their reactivities are essentially identical. In contrast, epoxidized soybean oil despite its higher epoxide content, not only is substantially less reactive, but the polymerization proceeds to lower conversion. It is interesting to speculate on the reasons for the divergent behavior of the three oils.

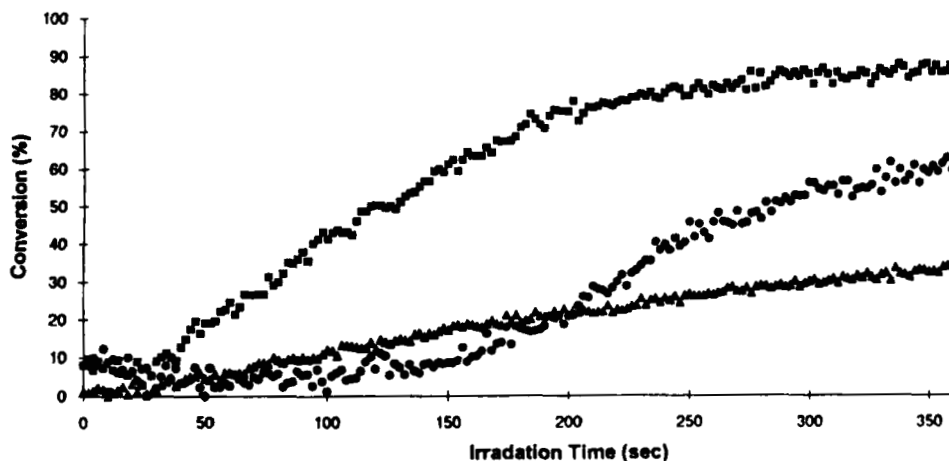


Figure 4. Comparison of the the photopolymerizations of \blacksquare , *Vernonia galamensis*, \bullet , *Euphorbia lagascae* and \triangle , epoxidized soybean oils with 2% IOC10 as photoinitiator.

In the two naturally epoxidized oils, which in addition to trivernolin, are composed of a mixture of triglycerides, including those with no, one, or two epoxyacyl groups per glycerol moiety, all the epoxy groups occur at the same position along the chains of the vernolic acid residues. In contrast, soybean oil contains oleate, linoleate and linolenate residues. When this oil is epoxidized, epoxy groups are dispersed at different positions along the chains. This may reduce the amount of intramolecular reaction in this oil and lead to inefficient consumption of epoxy groups during polymerization. The higher epoxide content of epoxidized soybean oil may also lead to early gelation and vitrification at low conversions resulting in the trapping of unreacted epoxy groups within the matrix.

CONCLUSIONS

Naturally occurring epoxidized triglyceride oils are interesting new monomers, which can be used to produce crosslinked polymers. In this

communication we have demonstrated that these oils undergo rapid, efficient cationic photopolymerization in the presence of typical diaryliodonium salt photoinitiators. Differences between the response of the two naturally occurring epoxidized triglyceride oils depends primarily on their purity. Further developments in isolation and processing techniques should considerably improve the performance of *E. lagascae* oil in photoinitiated cationic polymerization. These novel monomers hold considerable promise for such applications as UV curable coatings, inks and adhesives because of their potential low cost, volatility and toxicity.

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